Emerging Nanotechnology-based Corrosion Control Coatings

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Emerging Nanotechnology-based Corrosion Control Coatings

Outline:

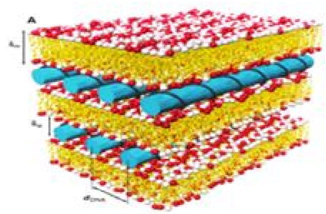
- The Impact of nanotechnology
- Application in Corrosion Control Coatings

Nanotechnology

Nanotechnology – the use of nano-sized materials to produce macro-sized products

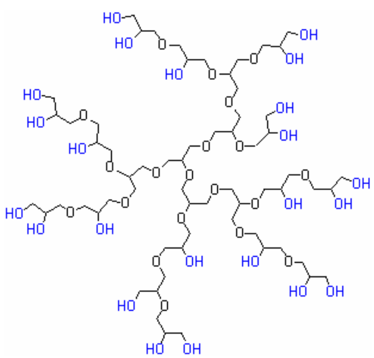
- The problem with this definition is that most of chemistry, materials physics and a sizeable fraction of materials engineering and biochemistry would fall within this definition

Nanoscience is being touted as the engine that will drive the next industrial revolution



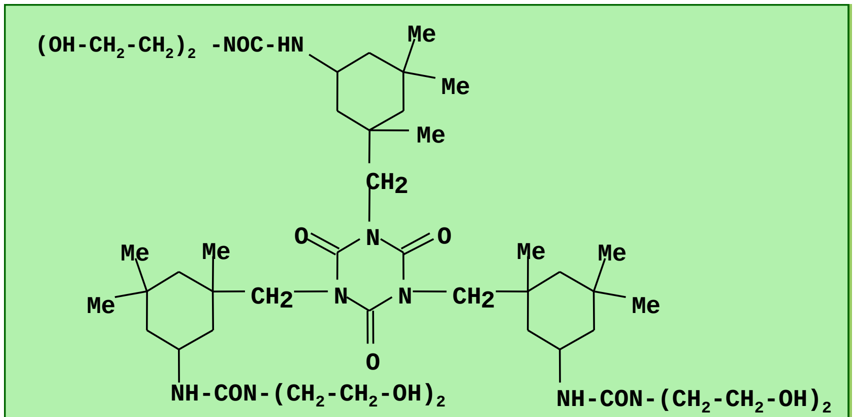
Nano-scale and Conventional Materials

Latex particle size	10 – 1000 nm
TiO_2 pigment particle	200 – 500 nm
Polyurethane dispersion	50 – 100 nm
Dissolved polymers	2 – 100 nm
Organic molecules	0.2 – 5 nm



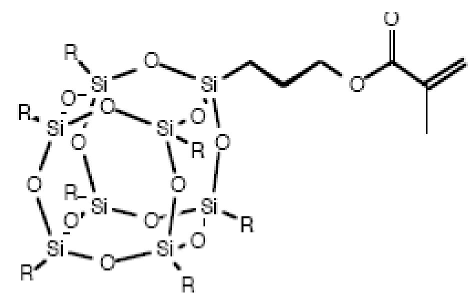
0.37 nm

Hydroxyl functional
Polyether dendrimer



0.70 nm

Hydroxyl functional IPDI-based dendrimer
J. Baghdachi, *et al*



0.51 nm

Methacrylate functional
silsesquioxane

Nano-materials

Aluminum oxide
Barium oxide
Carbon black
Calcium carbonate
Carbon nanotubes
Cerium oxide
Dendrimers, hyperbranched and supramolecules
Indium tin oxide
Nano-clays
Organic polymers
Silicone dioxide
Titanium dioxide
Zinc oxide

US Patents

1991-1995 – 4000
2001-2005 – 17,000

…and many more

Nanotechnology

Engineering and Technical contributions to-2008

- **Solid state physics**
  - Device miniaturization
  - Thin films
  - Photonics
  - Sensors
- **Biomedical**
  - Drug delivery

Coatings

Nanotechnology has fueled vigorous research and development in overlapping areas.

Why Nano?

◊ Control of coating composition on a molecular level

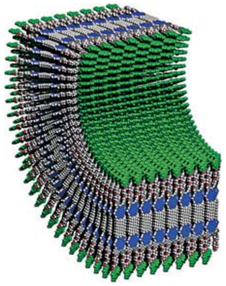
-Well-defined composition: "bottom up"

Major areas of Impact

- **Barrier**
- **Corrosion**
- **Antimicrobial**
- **Self-cleaning**
- **Superhydrophobic**

-More predictable behavior

-Novel properties



Cross section of a nanotube photoconductor

Nanotechnology in Coatings (--to 2008)

Technology	Material	Application	Time-to-market
Nano-particulate Coatings	ZnO, Al_2O_3	Exterior Automotive	Current-3 yrs
	Ce (III)	Corrosion control	Current-5 yrs
	Ceramics	Fuel cells	1-5 yrs
%Effort 95	Silver, Aluminum	Glass coating	Current-3 yrs
	Teflone™	Self-cleaning	Current-3 yrs
	Aniline/Polypyrrole	Super barriers	Current-3 yrs
		Drug eluting	1-3 yrs
Polymeric Nano-materials	Supramolecules	Topcoat	2-3 yrs
	Dendrimers &	Corrosion control	2-5 yrs
%Effort 5	Hyperbanched	Aerospace component	2-3 yrs
	Hybrid		

Nanotechnology-based Coatings

Materials and Applications

- **Corrosion Control**

Strategies for Corrosion Control by Coating

Protect metal from:

- Oxidation and dissolution
- Prevent electrolyte from reaching the metal surface or keep the concentration at a low level
- Limit water and oxygen transport to the metal
- Interfere with the corrosion reaction
- If corrosion does begin, prevent or reduce its spread

Strategies for Corrosion Control by Coating

Successful Impact

- Cost effective
- Safety
- Material compatibility
- Storage stability

In formulating a coating, one usually, makes certain compromises.

Nanotechnology Approaches

- Conventional Polymers
- Sol-gel Technology
- Inherently Conductive Polymers
- Stimuli responsive/Smart coatings

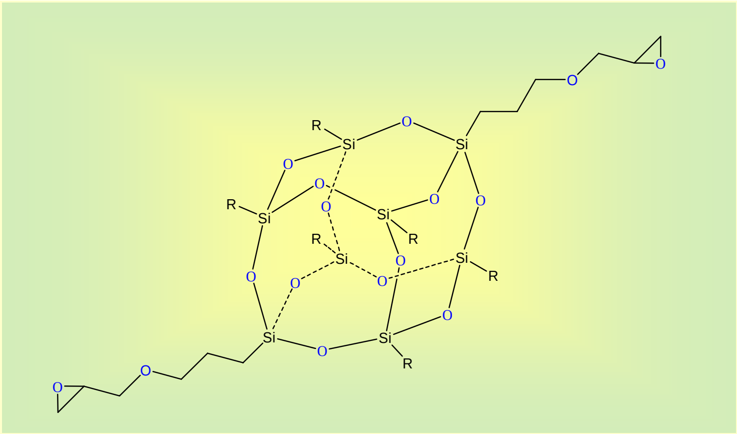
Nanotechnology-based Corrosion Control Coatings

- Polymer nanocomposite coatings, Al_2O_3, Fe_3O_4, Ce $(NO_3)_3$, etc.
  wang Y., et al, *Wear*, **260**, 976-983, 2006.

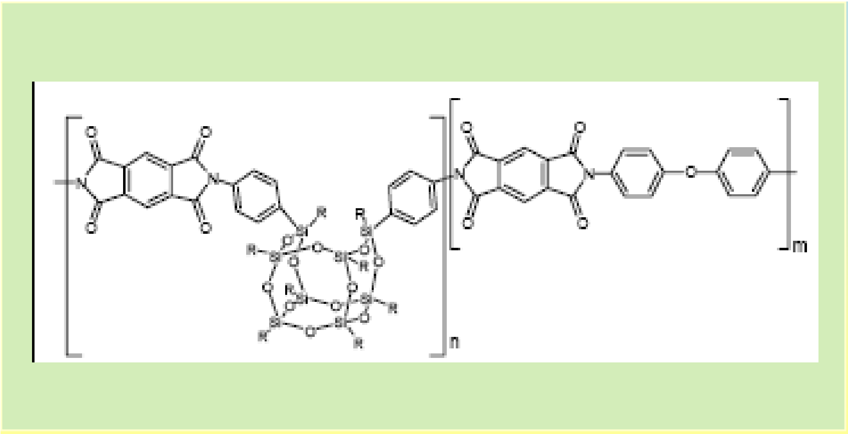
- Epoxy systems with dispersed polyaniline nanoparticles
  Wessling, B and Posdorfer, J., *Synth. Met.,* **102**, 1400-1401, 1999.

- Fluoro- and silicon/silicone modified polymers

- Organic-inorganic hybrid polymers

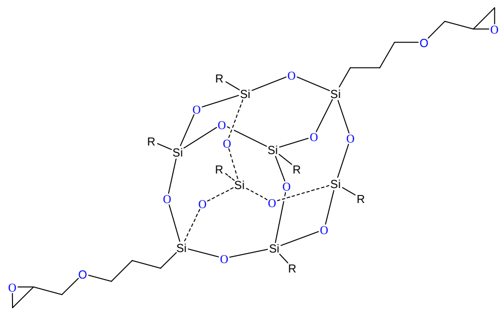


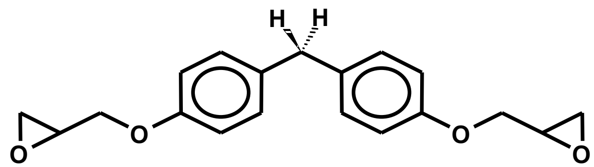
Baghdachi, et al, Smart Coatings, 2008



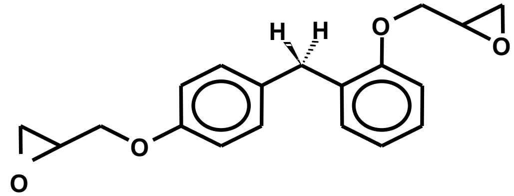
Hopkins, A, The Aerospace Corporation

Nanotechnology-based Corrosion Control Coatings





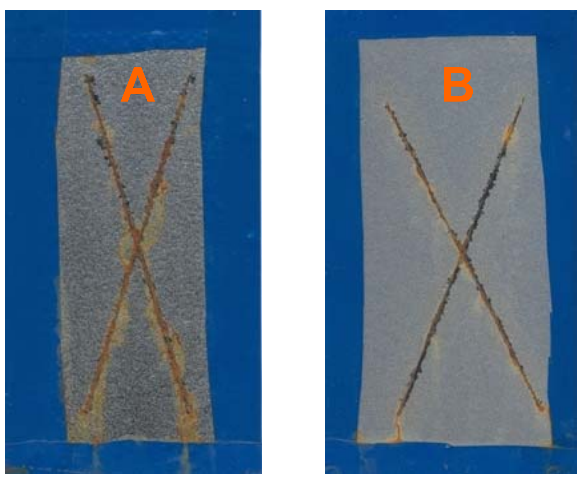
4,4' Isomer



2,4' Isomer

Cycloaliphatic Amine

35% 65% + 100%

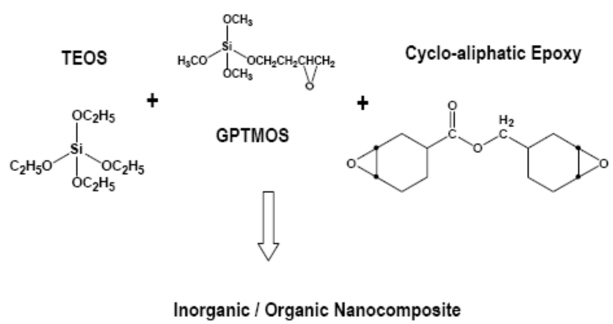


ASTM B117 testing: A, no POSS; B, with POSS after 680 hrs

Corrosion resistant epoxy primer base

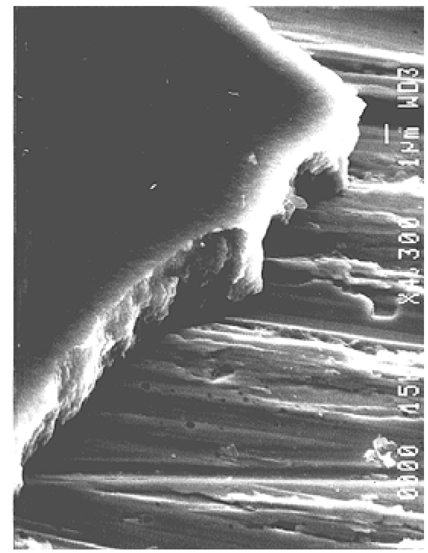
Sol-gel Technologies

Self-Assembled Nanophase Particle technology "SNAP" can produce thin diffusion barrier coatings



Advantages
- Barrier properties
- RT process

Limitations
- Porosity
- Crack formation
- High bake temp.



Sol-gel silica coating, 3 μm thick on high temperature alloy

http://www.solgels.com/

Sol-gel Technologies

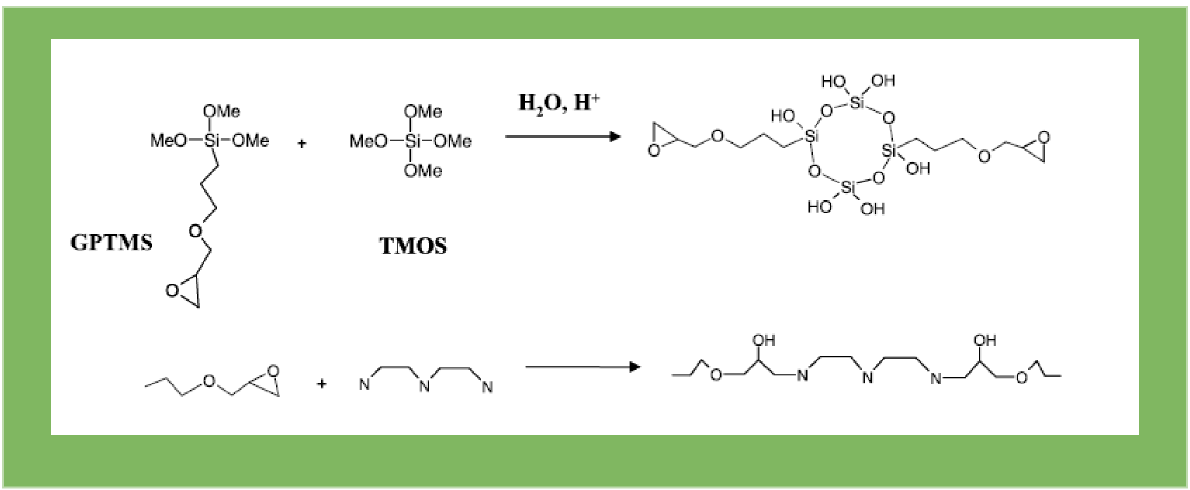
Technology Improvements

- Corrosion inhibitor additives

  Zheludkenich, M., et al *Surf. Coat Technol*., **200**, 3084-3094, 2006
  Zheludkenich, M., et al *Electrochim Acta*, **51**, 208-217, 2005
  Ferreira, M., et al *Electrochim Acta* **49** 2927-2935, 2004

- Barrier property improvement

- Khramov, A., et al *Prog. Org. Coat.* **47**, 207-213, 2003



ZrO_2

Ce^{+3}

La^{+3}

Aminosilane crosslinker

Sol-gel Technologies

Technology Improvements

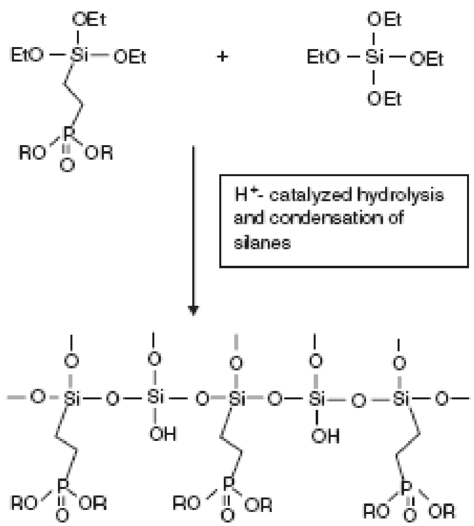
- Self-healing effect
  Khramov, A., et al *Thin Solid Films..*, **483**, 191-196, 2005
  Aparicio, M., et al *Corros. Sci.*, **50**, 1283-1291, 2008
  Kendig, M., *Prog., Org., Coat.*, **47**, 183-189, 2003

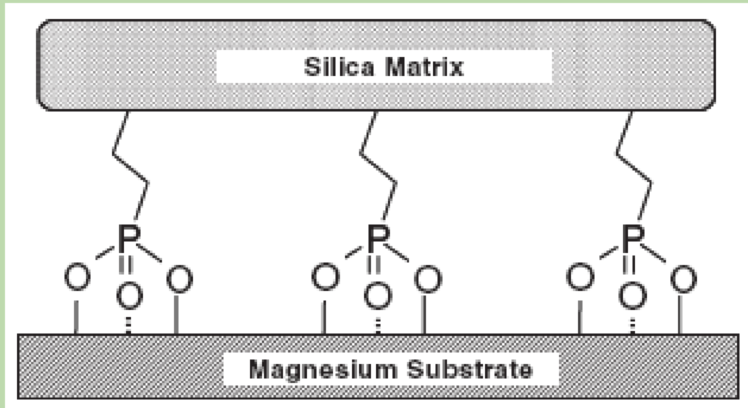
Organic Corrosion Inhibitors

Ce (III)

Polyaniline

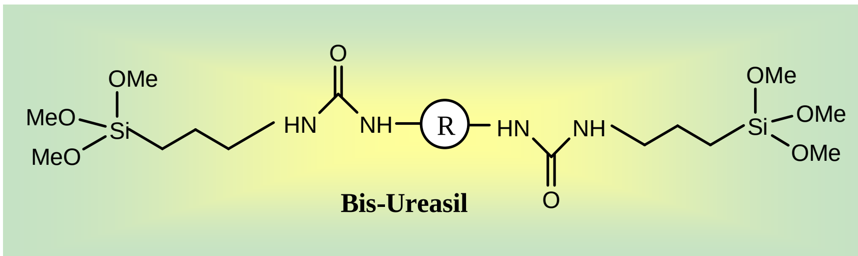
- Functionalization





Khramov, A., et al *Thin. Solid. Films.* **514**, 174-181, 2006

Hybrid Organic-Inorganic Sol-gel Coating



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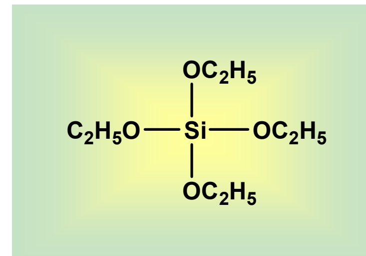
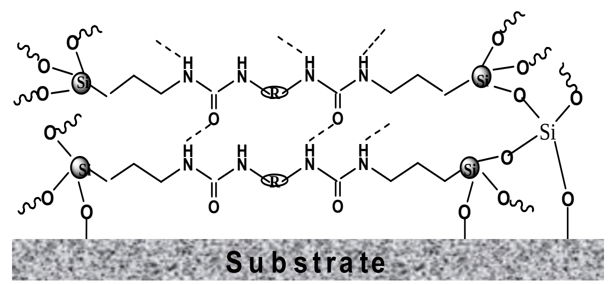


10 P	0 P	7 P
Alodine™ 1200S	Control	CRI Sol-gel
1000 hrs	24 hrs	1000 hrs

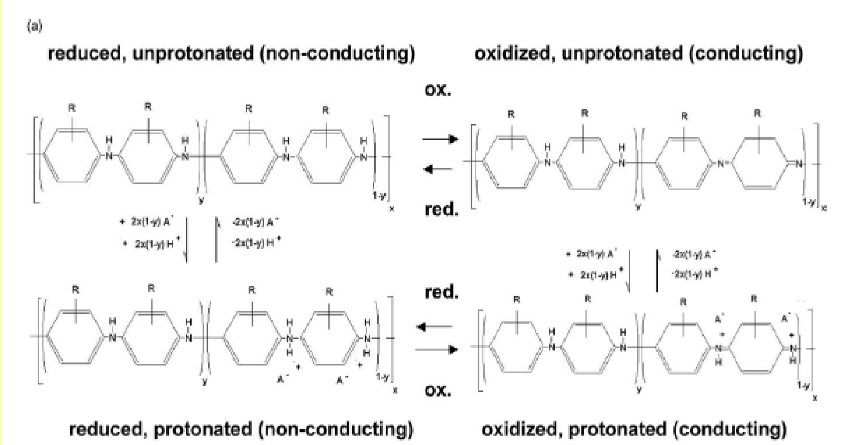


Mannari, V., et al, Eastern Michigan University

Evaluation: as per SSPC – Vis 2 (Pinpoint rusting standard)

Inherently Conductive Polymers

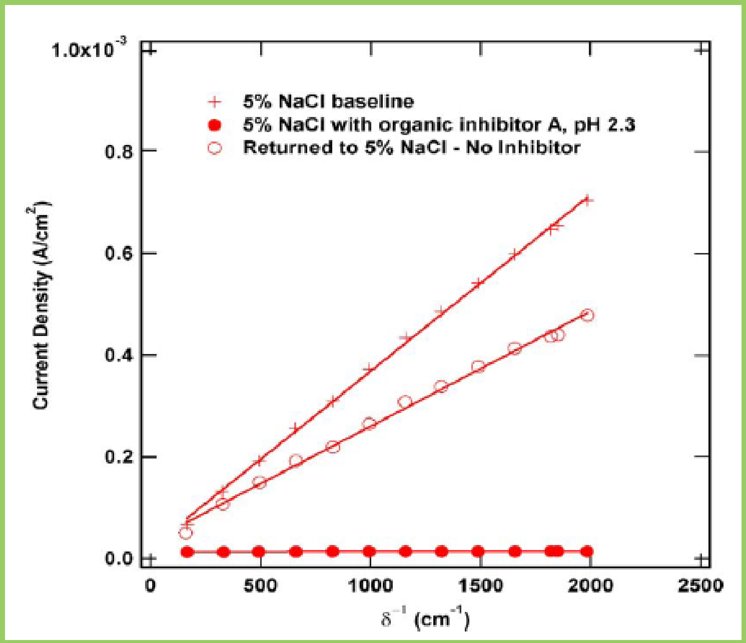
Coatings containing polyaniline in various doped or undoped states increase the corrosion resistance



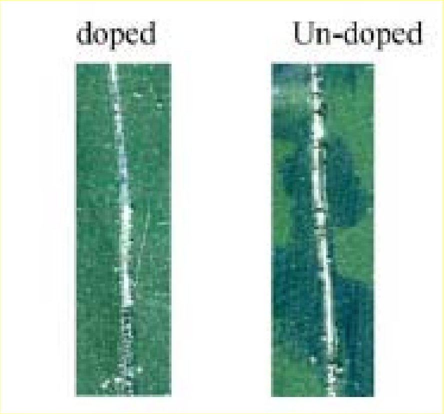
Polyaniline pigmented coatings on steel are highly corrosion resistant in both neutral and acidic media

Talo A. et al, *Synth. Met.* **102** 1394-1395, 1999
Azim, S., et al. *Prog. Org. Coat*., **56**, 154-158, 2006
Holness, R. et al. *J.Electrochem. Soc*., **152** (2)73-81, 2005

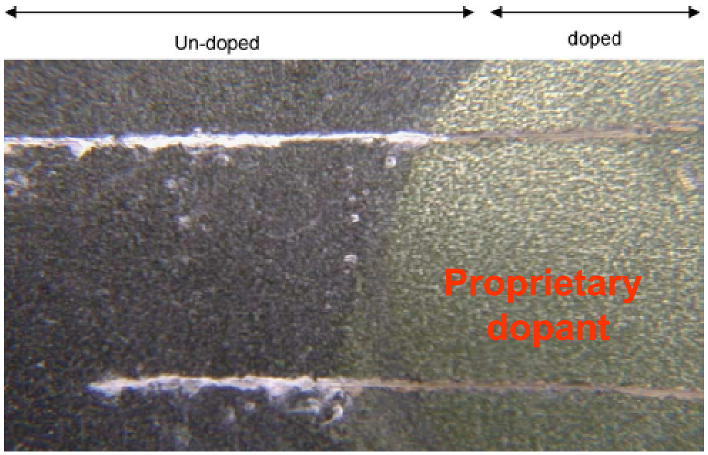
Inherently Conductive Polymers "Self-healing"



Plot of current density vs. inverse length
for a Cu RDE in aerated 5% NaCl



Commercial

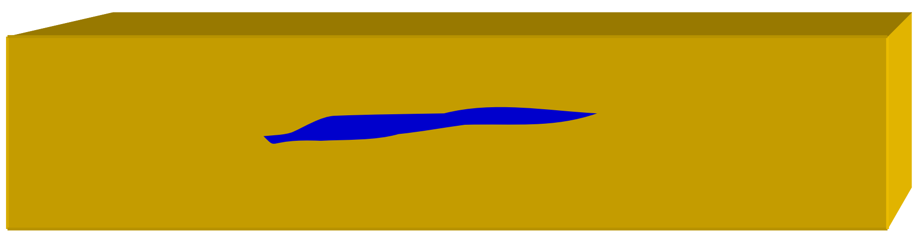


Kendig, M., *Prog., Org., Coat.*, **47**, 183-189, 2003

Self-healing Coatings

- Self-healing in most polymeric systems is achieved by certain morphological tuning or by incorporating stimuli responsive functional materials within the matrix

- Self-healing materials, when damaged, are designed to sense failure, and respond to restore structural integrity



Baghdachi, J., ACS Symposium Series 964, 2008

Self-healing Coatings

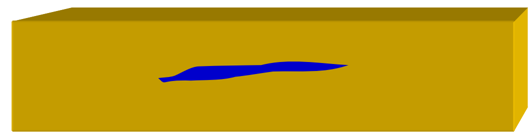
➢ Healing Mechanisms

S. White, et al. Univ. of Il

Mechanical forces

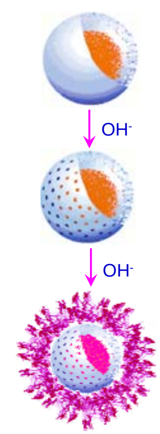
J. Baghdachi, et al. EMU

Elements of weathering



L. Calle, et al, NASA

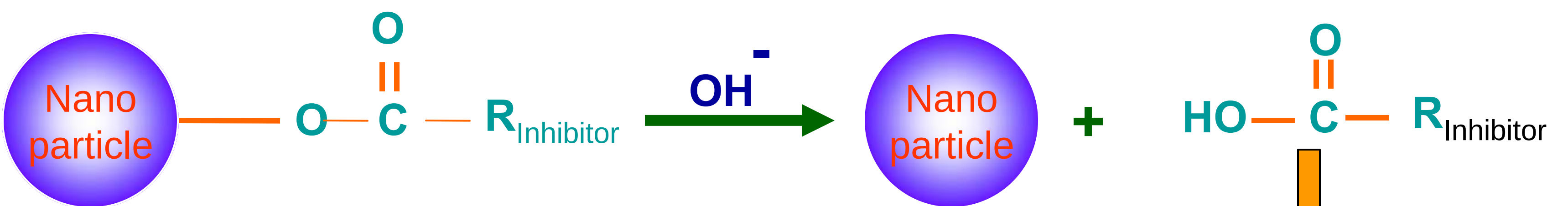
Corrosion by product

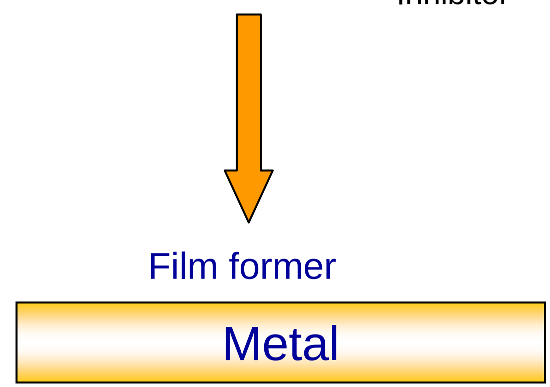


Nanomaterials as Corrosion Inhibitor Components

At the Anode: $Fe \rightarrow Fe^{+2} + 2e$

At the Cathode $O_2 + 2H_2O + 4e \rightarrow \mathbf{4OH^-}$





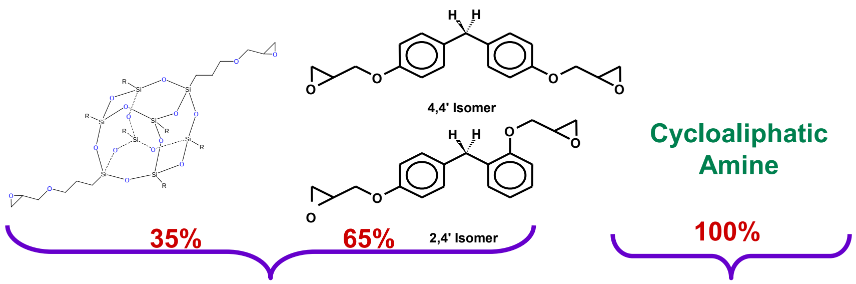
- Corrosion undergrowth in Coating MIL-DTL-24441
  - No corrosion under coating with TDA Coating

TDA Research

Cook, R. TDA Research, www.tda.com

Nanotechnology-based coatings

Corrosion resistant Hybrid Organic-Inorganic Coatings



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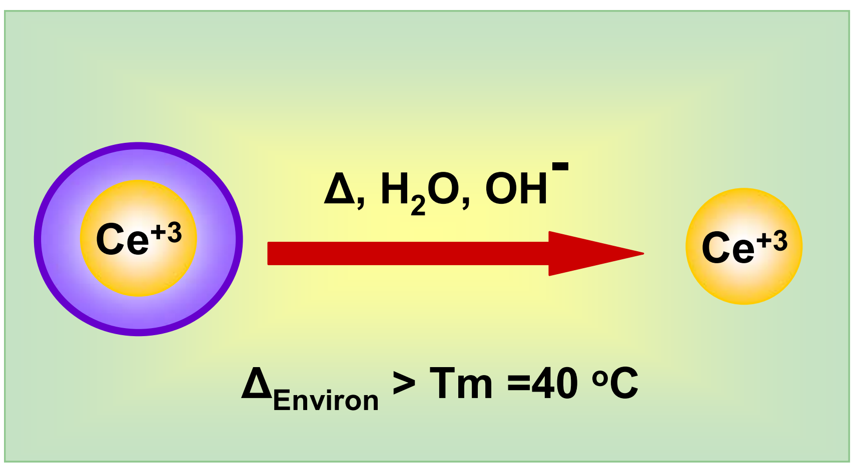
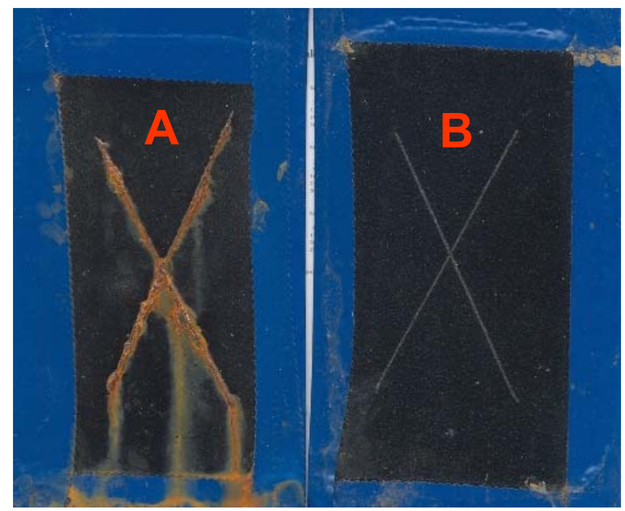




ASTM B117 testing: A, control; B, with healing agent after 960 hrs

Coatings Research Institute

Nanotechnology-based coatings

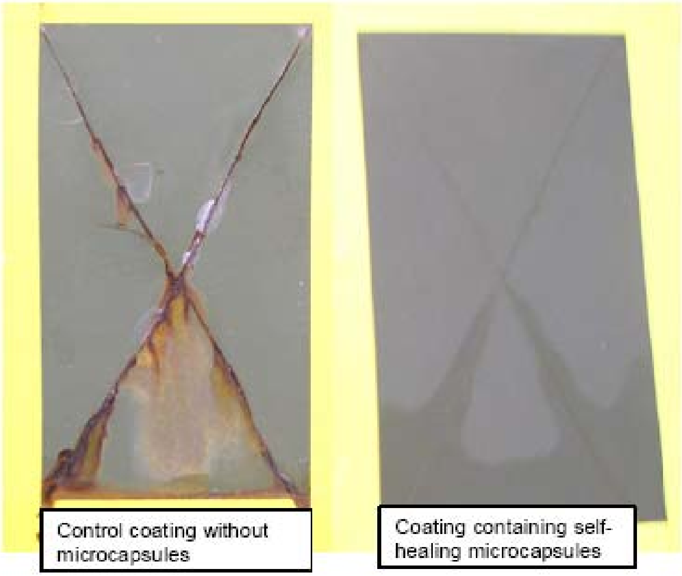
Self-healing Coatings for Corrosion Control

Phenolic varnish plus corrosion inhibitors

Stephenson, L, et al *US 2008/0152815*

Air drying triglyceride plus corrosion inhibitor.

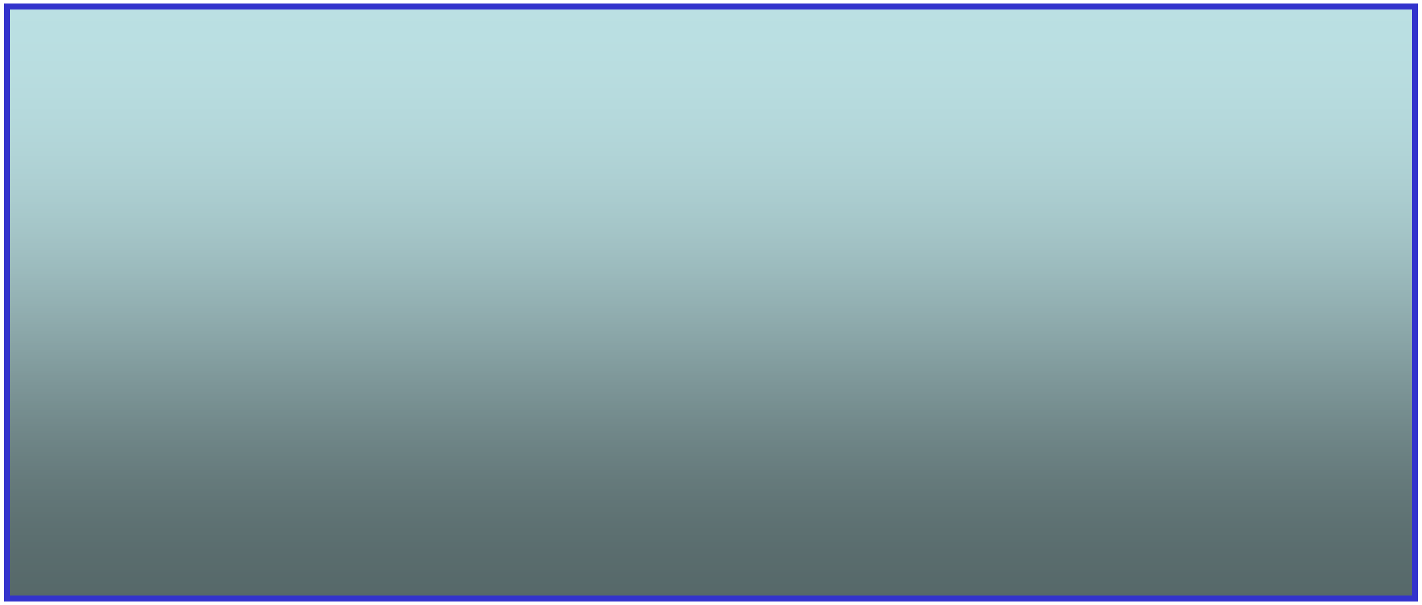
Koene, B., et al, *Proc. Self-healing Conf. 2007*



Luna corporation

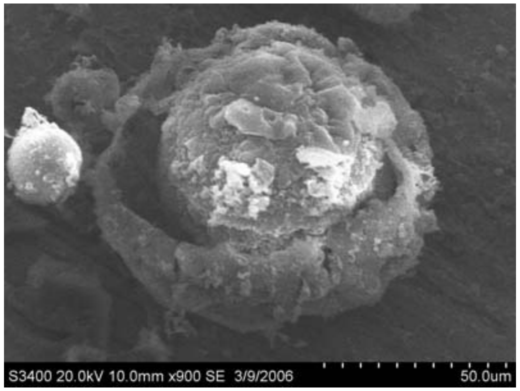
Stimuli Responsive Coatings

Self-healing is triggered by the elements of the weather

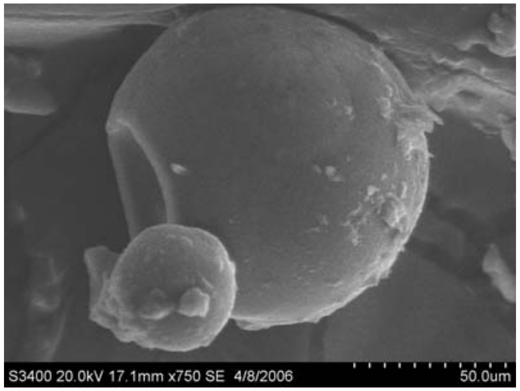


The factors that cause the most damage to the coating also initiate self-healing process.

Approach

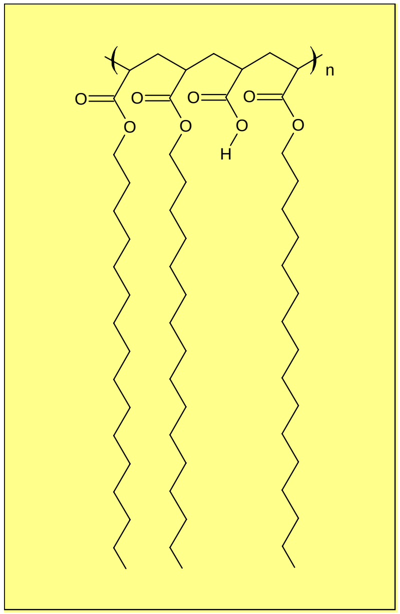


Microcapsule with
Bisphenol A epoxy



Microcapsule with
Ketimine

Selected SEM images of various microcapsules



Schematic representation of
chemical structure of shell polymer

Matrix composition:

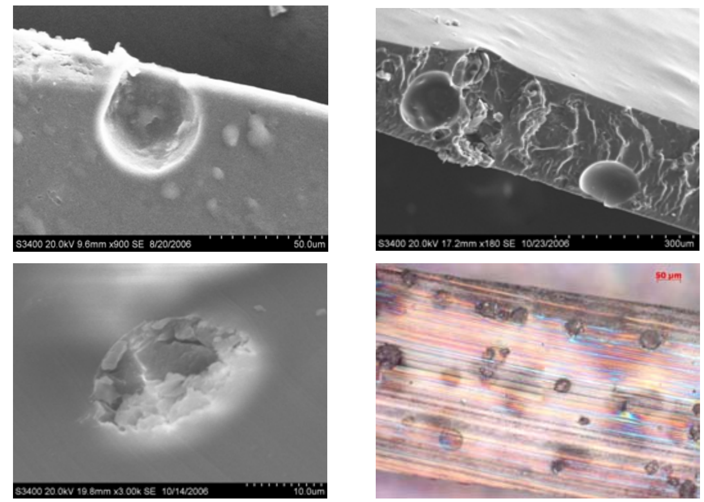
Bisphenol F resin
Cycloaliphatic amine

Self-healing Coatings

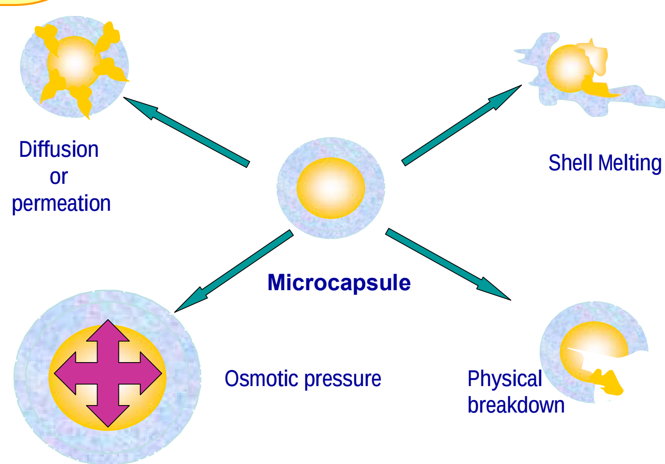
Methods and Mechanisms

Microcapsule rupture and healing agent release is triggered by:

T> Tm
Diffusion through porous shell
Diffusion of water
Osmotic pressure

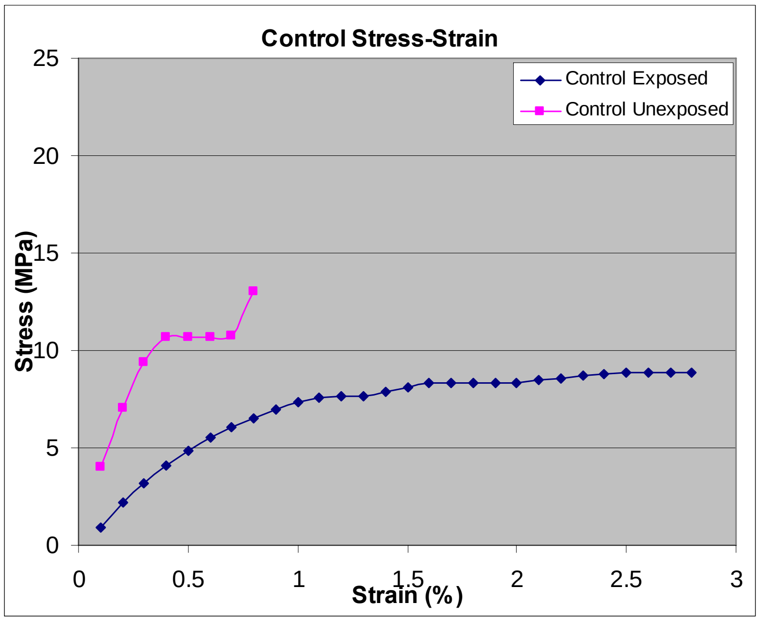


SEM and optical microscopy images of cross-section of self-healing coating

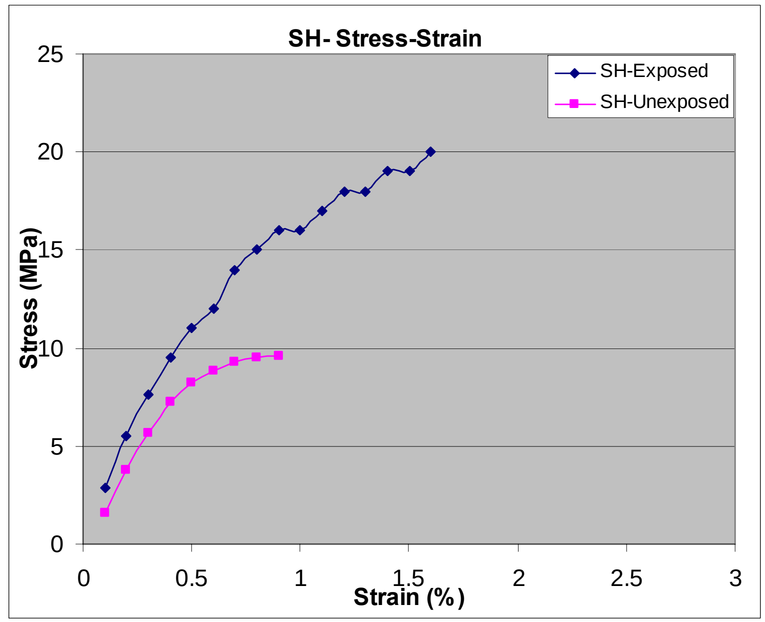


Self-healing Coatings

Dynamic Mechanical Analysis: Stress/Strain



a



b

Control without healing agent (a), -■-Control unexposed, -◆- Control exposed at 65-70% RH, 40-45 ^{o}C; sample with healing agent (b), -■- SH-unexposed, -◆- SH-exposed.

Self-healing Coatings

Corrosion Testing, ASTM B117

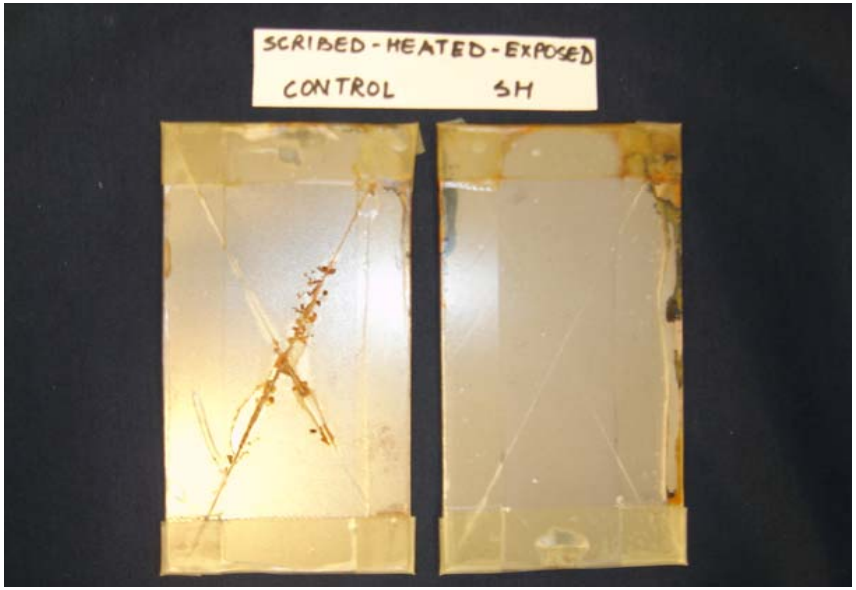
Objectives

- Confirm self-healing function
- Confirm corrosion resistance improvement

-Scribed/Exposed, (XE)
-Scribed/Heated (40 ^{o}C/10 min)/Exposed, (XHE)
-Heated 40 ^{o}C/Scribed/Exposed, (HXE)
-Scribed/E100 hrs/ Heated10 min/Exposed, (XEHE)

Self-healing Coatings

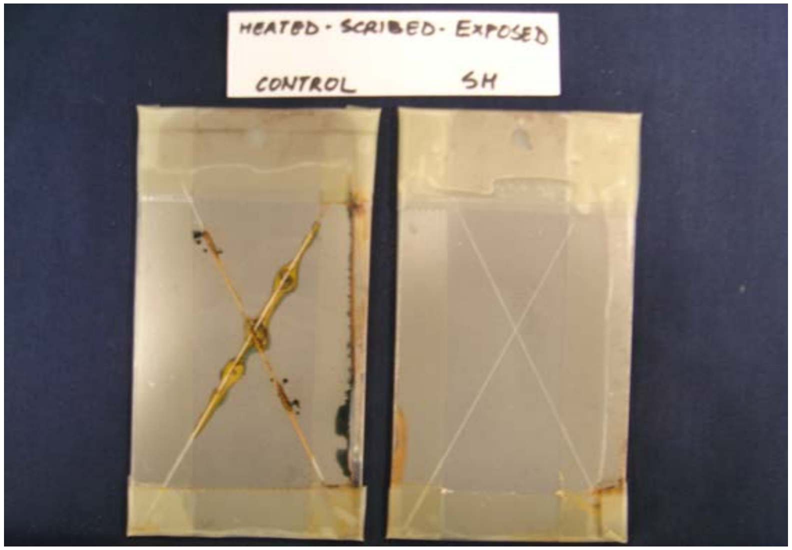
ASTM B117



- Self-healing samples showed no corrosion at 666 hrs
- Control samples corroded after 480 hrs
- Evidence of corrosion at 684 hrs on self-healing samples

Self-healing Coatings

ASTM B117



- Control with or without heat treatment fails corrosion testing
- Heat treatment of damaged coating with healing agents enhances corrosion resistance

Nano Safety

- **Nanotechnology**, like any new technology, comes with risks

- Nanomaterials may possess the toxicity of both the bulk forms and the activity and interactions of nano-sized chemicals

- Increased surface-to-volume ratio of nanoparticles may result in:
  - -Ingestion through cell membrane
  - -Sensitivity to shape of nanoparticles
  - -Adhesion to cell surface


Summary

- The revolutionary properties of nanomaterials provide evolutionary properties to coatings
- Nanotechnology approaches have resulted in coatings with improved adhesion and barrier and corrosion resistance
- Research and development in coatings has been fueled by nanotechnology.
- Nano-engineered and smart coatings provide the basic function of coatings and achieve results that cannot be attained in any other way.

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